

Regularities of Cu, Pb and Zn adsorption by chernozems of the South of Russia

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Abstract

The parameters of Cu²⁺, Pb²⁺ and Zn²⁺ adsorption by chernozems of the south of Russia and their particle-size fractions were studied. The adsorption capacity of chernozems for Cu²⁺, Pb²⁺, and Zn²⁺ depending on the particle-size distribution decreased in the following sequence: clay loamy ordinary chernozem ~ clay loamy southern chernozem > loamy southern chernozem > loamy sandy southern chernozem. According to the parameters of the adsorption by the different particle-size fractions (C_{max} and k), the heavy metal cations form a sequence analogous to that obtained for the entire soils: Cu²⁺ ≥ Pb²⁺ > Zn²⁺. The parameters of the heavy metal adsorption by similar particle-size fractions separated from different soils decreased in the following order: clay loamy chernozem > loamy chernozem > loamy sandy chernozem. The ratio between the content of exchangeable cations displaced from the soil adsorbing complex (SAC) into the solution and the content of adsorbed HMs decreased with the increasing concentration of adsorbed HMs. These values could be higher (for Cu²⁺ and Pb²⁺), equal, or lower than 1 (for Zn²⁺) and depend on the properties of HMs. At the first case, this was due to the dissolution of readily soluble salts at low HM concentrations in the SAC. In the latter case, this was related to the adsorption of associated forms HMs and the formation of new phases localized on the surface of soil particles at high HM concentrations in the SAC.

Keywords: adsorption, exchangeable cations, particle-size fractions, heavy metals

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Introduction

Ion-exchange adsorption phenomena are important in the immobilization of heavy metals (HMs) by soils. Numerous works are devoted to the study of this problem. However, the interaction features of different particle-size soil fractions and their role in the immobilization of HMs studied insufficiently. Therefore, the assessment of the effect of the particle-size distribution on the adsorption properties of soils is a vital task. In spite of the somewhat arbitrary nature of the methods for the analysis of the soil particle-size distribution and the boundaries of the particle-size fractions, they at large reflect the existing differences in the composition and properties of their particles. In the study of the soil's dispersion, attention is focused on the content of clay (as sum of silt <1 μm and dust 1-10 μm) and sand, because these data are used for the classification of soils according to their particle-size distribution.

The sand fraction includes the particles from 10 to 1000 μm. It mainly consists of quartz and small amounts of amphiboles and feldspars. These components play the role of a mechanical diluter for the substances mainly concentrated in the fractions <10 μm (Kryshchenko et al., 2008). The mineral components of the

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sand fraction are relatively inactive. Perelomov, Pinskiy (2003) found that the changes in the physicochemical properties of soils at the addition of 50 % washed sand under soil contamination with zinc significantly affected the fractional composition of the metal and increased its biological availability. As a result, the percentage of the exchangeable zinc fraction increased, and that of its residual fraction decreased. This was related to the fact that the surface of SiO₂ particles is a stronger Lewis base compared to soil particles covered with iron hydroxide and organic matter shells and less strongly retains Zn²⁺ (McBride, 1989).

The silt and dust fractions are the most dynamic and active soil components. The silt fraction mainly contains secondary mineral components: clay minerals, coagels, iron and aluminum oxides, allophanes, mono- and polysilicic acids, and organic and organomineral compounds. It is characterized by a high adsorption capacity for HMs and exogenic organic substances. According to the sorption capacities of the iron and clay minerals in the clay fractions, the HM cations form the following sequence: Cd²⁺ > Pb²⁺ > Cu²⁺ > Zn²⁺ (Manceau et al., 1996). According to the strength of the ion retention by the clay fraction's surface, these elements form a different sequence: Pb²⁺ > Zn²⁺ > Cu²⁺ > Cd²⁺.

The heavy metals have capacity to specific adsorption by soils as opposed to cations of alkaline metals. Since adsorption of heavy metal cations by soils has ion-exchange character, investigation of reversibility and balance of this process represent interest also.

The aim of this work is to study the effect of the particle-size distribution, the clay and silt on the adsorption of copper, lead, and zinc by chernozems of the south of Russia and the balance between adsorbed HMs and displaced exchangeable cations.

Material and Methods

The objects of study included the upper humus horizons of a medium-deep clay loamy calcareous southern chernozem on yellow-brown structural clays, a medium-deep loamy southern chernozem on yellow-brown loess-like loams, a medium-deep loamy sandy southern chernozem on sands, and a medium-humus clay loamy calcareous ordinary chernozem on loess-like loams from Rostov oblast (Table 1).

Table 1. Physical and chemical properties of the soils studied (0-20-cm Ap horizon)

Parameter	Clay loamy	Southern chernozems		
	ordinary chernozem	clay loamy	loamy	loamy sandy
Clay, %	48.1	53.9	31.4	12.4
Silt, %	28.6	31.0	19.1	8.0
Humus, %	4.2	3.9	3.5	3.5
pH	7.3	7.4	7.5	7.2
CaCO ₃ , %	0.12	0.45	–	–
CEC, meq/100 g	36.1	36.1	31.8	25.9

The content of humus was determined by the Tyurin method modified by Simakov, the cation exchange capacity (CEC) was determined by the Bobko–Askinazi method, the available phosphorus and exchangeable potassium were determined by the Machigin method, the pH was determined by potentiometry, and the carbonates were determined by the Kudrin method (Sokolov, 1975). The exchangeable cations were determined by the Shaimukhametov method (Shaimukhametov, 1993).

The analysis of the particle-size distribution and the separation of the silt and clay were performed by the pipette method after the pyrophosphate treatment of the samples (Vadyunina and Korchagina, 1986). To study the ion-exchange adsorption of the Cu²⁺, Pb²⁺, and Zn²⁺ cations, the soil in the natural ionic form was disaggregated using a pestle with a rubber head and sieved through a 1-mm sieve. The soil samples were treated with solutions of Cu²⁺, Pb²⁺, and Zn²⁺ nitrates. The concentrations of the initial solutions varied in the range from 0.05 to 1 mM/l. The soil:solution ratio was 1:10. The suspensions were shaken for 1 h, left to stand to 24 h, and filtered. The contents of HMs in the filtrates were determined by atomic absorption spectroscopy. The contents of adsorbed HM cations were calculated from the difference between the metal concentrations in the initial and equilibrium solutions. Each point of the experimental isotherms was found in triplicate.

The isotherms had a form described by the following Langmuir equation:

$$C_{\text{ads.}} = C_{\text{max.}}kC/(1 + kC), \quad (1)$$

where: C_{ads} is the content of the adsorbed cations; C_{max} is the maximum adsorption of the HM, mM/100 g of soil; k is the constant of the affinity; and C is the HM concentration in the equilibrium solution, mM/l.

The approximation of the experimental isotherms by the Langmuir equation was performed using the SigmaPlot 2001 statistics package at a confidence probability of 0.95.

Results

The isotherms of the HM adsorption by the ordinary chernozem and southern chernozems are shown in Fig. 1; the parameters of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by the soils studied are given in Table 2.

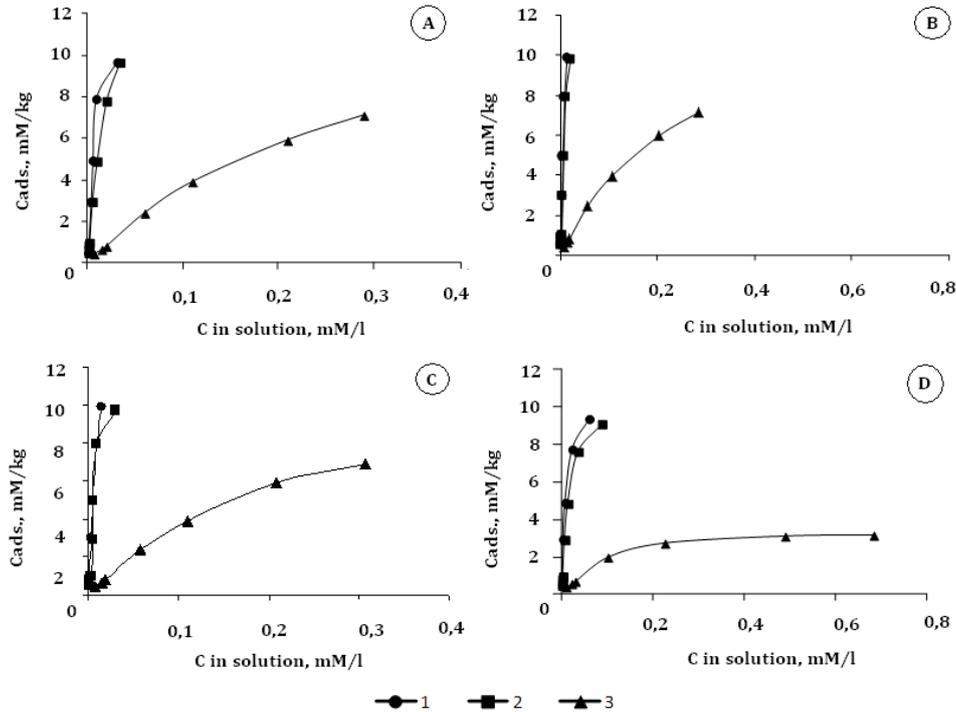


Figure 1. Isotherm adsorption of Cu, Pb and Zn by clay loamy ordinary chernozem (A) and southern chernozems: clay loamy calcareous (B), loamy (C) and sandy (D).

Table 2. Parameters of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by chernozems with different particle-size distributions

Adsorption parameters	Cu^{2+}	Pb^{2+}	Zn^{2+}
<i>Clay loamy ordinary chernozem</i>			
C_{max} , mM/kg	13.3 ± 1.30	14.55 ± 0.60	14.55 ± 0.60
k , l/mM	93.72 ± 20.69	40.89 ± 4.87	3.28 ± 0.21
R^2	0.94	0.93	0.99
<i>Clay loamy southern chernozem</i>			
C_{max} , mM/kg	23.66 ± 3.54	21.15 ± 5.90	13.48 ± 0.48
k , l/mM	58.25 ± 13.20	47.13 ± 17.11	4.09 ± 0.35
R^2	0.99	0.96	0.99
<i>Loamy southern chernozem</i>			
C_{max} , mM/kg	20.59 ± 9.16	16.57 ± 5.39	12.55 ± 0.59
k , l/mM	54.54 ± 21.92	34.80 ± 12.73	3.95 ± 0.25
R^2	0.99	0.88	0.98
<i>Loamy sandy southern chernozem</i>			
C_{max} , mM/kg	19.01 ± 1.02	14.65 ± 1.19	11.05 ± 0.93
k , l/mM	25.90 ± 2.36	21.83 ± 3.44	2.63 ± 0.34
R^2	0.95	0.97	0.99

The general shapes of the isotherms of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by the silt and clay from the southern chernozem were analogous to those of the HM adsorption by the entire soil: the adsorption was of limited character and followed the Langmuir equation (Fig. 2, 3). Copper and lead were more intensively adsorbed by the particle-size fractions than the zinc.

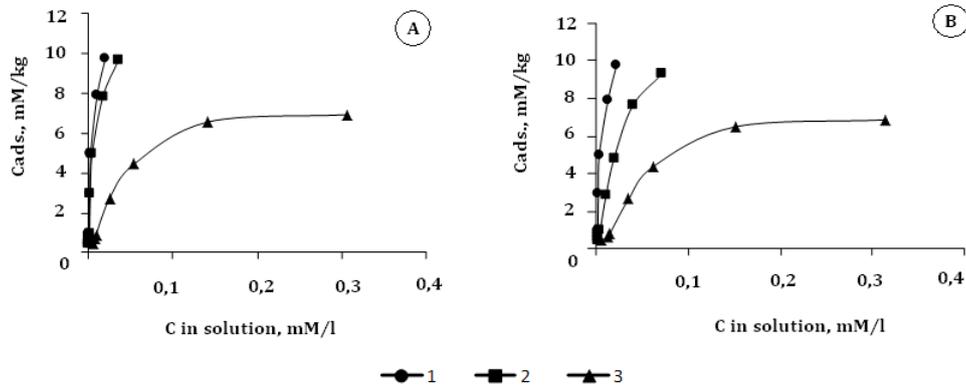


Figure 2. Isotherms of Cu^{2+} (1), Pb^{2+} (2), and Zn^{2+} (3) adsorption by clay (A) and silt (B) fraction of the clay loamy southern chernozem.

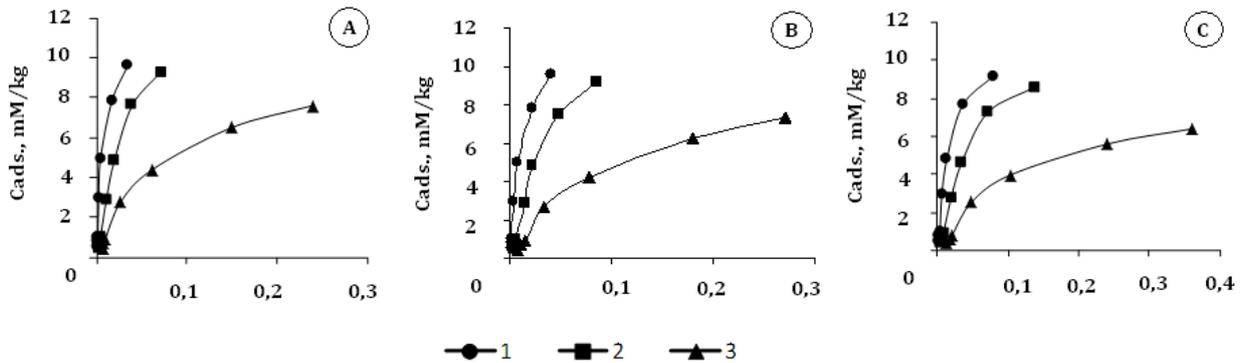


Figure 3. Isotherms adsorption of Pb^{2+} by soils (1), silt (2) and clay (3) of southern chernozems: clay loam (A), loam (B), and sandy (C).

In the particle-size fractions separated from the soils, the concentrations of Cu^{2+} , Pb^{2+} , and Zn^{2+} decreased with the decreasing particle size. The values of k and C_{max} characterizing the adsorption of HMs by the southern chernozem and its particle-size fractions formed the following sequence: silt > clay > entire soil (Tables 3, 4). A similar sequence was observed for the particle-size fractions of the ordinary chernozem (Minkina et al., 2009).

Table 3. Parameters of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by a clay loamy southern chernozem and its particle-size fractions

Adsorption parameters	Cu^{2+}	Pb^{2+}	Zn^{2+}
		<i>Silt</i>	
C_{max} , mM/kg	28,45±0,46	25,20±0,59	17,90±0,47
k , l/mM	80,20±20,29	65,90±16,14	18,65±3,00
R^2	0.99	0.99	0.99
		<i>Clay</i>	
C_{max} , mM/kg	22,15±1,22	20,40±2,15	12,50±1,96
k , l/mM	58,20±14,54	49,26±13,35	12,07±3,12
R^2	0.92	0.98	0.98
		<i>Soil</i>	
C_{max} , mM/kg	17,58±3,03	14,54±2,97	8,99±1,90
k , l/mM	38,80±12,33	30,45±11,96	4,94±0,63
R^2	0.95	0.96	0.94

Table 4. The coefficients of the binary correlation between parameters of the Cu, Pb, and Zn adsorption and the particle-size fraction and humus content in chernozem soils of the south of Russia

Metal	Silt		Clay		Humus in soil		Humus in clay	
	C_{max}	k	C_{max}	k	C_{max}	k	C_{max}	k
Cu	0,99	0,91	0,99	0,89	0,96	0,64	- 0,88	- 0,99
Pb	0,98	0,99	0,98	0,99	0,97	0,84	- 0,86	- 0,96
Zn	0,99	0,90	0,98	0,88	0,87	0,62	- 0,99	- 0,99

To assess the role of humus in the adsorption of HM cations by the soils and their particle-size fractions, the correlation coefficients (R) between the content of the adsorbed Cu^{2+} , Pb^{2+} , and Zn^{2+} ; and contents of clay and silt in the soils; and the humus under contamination of HM were calculated (Table 5).

Table 5. The coefficients of the correlation (R) between parameters of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by the soils; the particle-size distribution; and the humus content in the soils

Parameter	$R (C_{max})$	$R (k)$
Silt	0,98-0,99	0,90-0,99
Clay	0,98-0,99	0,88-0,99
Soils	0,83-0,97	0,62-0,89
Soil humus	0,83-0,97	0,62-0,89

Chernozem with a natural content of exchangeable cations was used in the experiments; therefore, the assessment of their participation in the sorption processes has of significant interest. The balance between of adsorbed HM cations ($C_{ads.}$) and displaced into solution Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and H^+ are given in Table 6.

Table 6. The balance of heavy metals adsorbed cations by ordinary chernozem and displaced exchangeable cations

Adsorbed HM, meq/kg	Displaced cations, meq/kg					$\Sigma disp. cat.$	$\Sigma disp. cat. ads. HM$
	Ca^{2+}	Mg^{2+}	Na^+	K^+	H^+		
				Cu(NO ₃) ₂			
1.00	2.4	0.2	0.04	0.007	0.001	2.65	2.65
1.58	2.4	1.40	0.17	0.012	0.001	3.98	2.52
1.98	3.4	1.60	0.38	0,013	0.001	5.40	2.73
5.94	7.8	3.20	0.46	0.013	0.002	11.48	1.93
9.90	11.0	4.20	0.72	0.016	0.002	15.94	1,61
15.82	15.6	5.00	1.4	0.08	0.007	22.09	1,40
19.38	17.4	6.00	1.5	0.24	0.009	25.15	1,30
				Pb(NO ₃) ₂			
0.98	2.0	0.36	0.18	0.06	0.001	2.06	2.1
1.58	2.4	0.5	0.17	0.08	0.002	3.15	1.99
1.96	2.4	0.4	0.25	0.15	0.002	3.2	1.63
5.9	6.2	1.8	0.6	0.30	0.003	8.9	1.51
9.8	9.8	3.4	1.0	0.45	0.004	14.65	1.5
15.6	14.0	5.0	1.8	0.96	0.005	21.77	1.34
19.32	15.0	5.8	2.0	1.10	0.006	23.91	1.24
				Zn(NO ₃) ₂			
0.86	1.8	0.6	0.03	0.008	0.001	2.44	2.83
1.3	2.0	0.6	0.12	0.001	0.001	2.72	2.09
1.6	2.0	1.0	0.19	0.014	0.001	3.21	2.0
4.8	4.4	1.8	0.29	0.015	0.001	6.51	1.36
7.8	6.8	2.2	0.33	0.015	0.002	9.35	1.2
11.8	7.4	2.6	0.48	0.06	0.003	10.54	0.89
14.2	10.0	2.6	0.50	0.08	0.003	13.18	0.93

Discussion

The analysis of the obtained data showed for the southern chernozems that a tendency toward a decrease in the maximum adsorption C_{\max} and the metal adsorption constants k was observed when going from the clay loamy to loamy sandy soils (Fig. 1). The tendency was more pronounced for the adsorption of Cu^{2+} and Pb^{2+} ions. The decrease in C_{\max} at the change of the particle-size distribution in similar soils is related to the known relationship between the specific surface and the adsorption capacity of the soils. For the southern chernozems, it varied in the following sequence: clay loamy > loamy > loamy sandy.

The tendencies toward regular changes in the parameters of the ion-exchange adsorption of the HM cations by the soils with different particle-size distributions can be due to the actual differences in the chemistry and mineralogy of the corresponding fractions of the studied soils and the ability of HMs to specifically interact with specific groups of exchangeable sites. In particular, the values of C_{\max} and k calculated from the isotherm of the Cu^{2+} adsorption by the clay loamy ordinary chernozem were found to be significantly lower than the corresponding values for the clay loamy southern chernozem, which could be related to the differences in the composition of the fine fractions manifested at the soil subtype level and the features of the Cu^{2+} 's interaction with the active sites on the surface of the soil particles.

Wong et al. (2007) studied the sorption of zinc by soils differing in acidity and particle-size. By the ability to sorb zinc cations, they formed the following sequence: calcareous clay soil > calcareous sandy soil > acid sandy laterite soil. This sequence indicated an important role of the particle-size distribution and the soil solution's pH during the sorption of metals.

The important role of organic matter in metal adsorption was noted in the works of Karpukhin and Sychev (2005) and Minkina et al. (2006, 2012). Data obtained by Plyaskina and Ladonin (2005) indicated that more than 50% of the copper and zinc in all particle-size fractions of a leached chernozem was bound to organic matter, and the remaining portion was strongly bound to the mineral soil components, including iron minerals. For zinc, the interaction with organic matter was less typical (Putilina et al., 2009). At the same time, a significant part of the surface of chernozem particles is covered with humus films. They have a complex effect on the adsorption capacity of the soil particles. They can hamper the contact of HM ions with reactive sites located on the surfaces of mineral soil components and in their medium and small pores and hydrophobize some surface areas, which resulted in a decrease in the exchange capacity of soils (Pinskii, Kurochkina, 2006). At the same time, new reactive sites can appear due to the functional groups of adsorbed organic molecules.

The reliable decrease in the value of k with the decreasing content of the fine fractions in soils cannot be explained only by the change in the specific surface of the soil particles. The constants characterize the energy of the cations interaction with the active sites on the surfaces and are mainly related to the qualitative composition of soil particles. Thus, the change in the adsorption constants with the variation in the particle-size distribution clearly indicates a difference in the qualitative composition of the fine fractions of the soils studied. Moreover, the k values depend more on the content of the fine fractions than the C_{\max} values.

When the studied soils are ranked according to the HM adsorption parameters, the following sequence is observed for the adsorption constants: clay loamy southern chernozem > loamy southern chernozem > loamy sandy southern chernozem. The values of C_{\max} for the adsorption of copper and lead little vary with the changes in the soils' particle-size distribution. However, the tendency toward a decrease in this parameter with decreasing contents of clay and silt is clearly traced. Thus, in this case too, the extensive adsorption parameter – the maximum adsorption – is less sensitive to changes in the particle-size distribution than the intensive parameter of the process – the constant of the adsorption equilibrium.

The clay, which includes silt and fine fractions (1-10 μm) is the main carrier of the soil's adsorption properties; therefore, given the quantitative and qualitative compositions of the soil, the further behavior of the HMs can be predicted. Therefore, the direct study of the HM adsorption by the separate soil particle-size fractions has a significant interest.

The separation of the particle-size fractions by the pipette method after the pyrophosphate treatment of the samples disturbs the natural composition of the exchangeable cations; therefore, the samples should be converted into the same state. For this purpose, the soil and its particle-size fractions were converted into the monoionic Ca form. The original soil sieved through a 1-mm sieve and the separated particle-size fractions were converted into the monoionic Ca forms by tenfold treatment with a 0.25 M $\text{Ca}(\text{NO}_3)_2$ solution.

Then, the soil was washed from excess salt with distilled water, air-dried, and homogenized. Samples of the soils and fractions were treated with tenfold volumes of solutions containing different amounts of HM nitrates with the addition of calcium nitrate to maintain a constant ionic strength of 0.01 mol/l. The further procedures were similar to those described above for the study of the HM adsorption by soils.

The works of some authors (Scheinov et al., 2002, Titova et al., 1996) carried out with different soil types showed that the saturation of the fine fractions by HMs decreased in the following sequence: silt > fine dust (1-5 μm) > medium dust (5-10 μm). The dust fraction contained 14.6% Cu^{2+} , 16.6% Pb^{2+} , and 12.6% Zn^{2+} on the average for all the soils (Zyrin and Chebotareva, 1989). On the average for all the soils but the krasnozems, the concentrations of Cu^{2+} , Pb^{2+} , and Zn^{2+} in the clay fractions were found to be 52, 38, and 162 mg/kg, respectively. Higher contents of HMs in these fractions were reported by Titova et al. (1996). It was noted that the dust and clay of the soils accumulated 25–65% of the Cu^{2+} , 35–95% of the Pb^{2+} , and 53–89% of the Zn^{2+} . The maximum concentration of Cu^{2+} was found in the dust fractions lower than 1.8 g/cm³ in density; that of Pb^{2+} was most frequently observed in the clay.

The differences in the parameters of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by the studied soils and their particle-size fractions are determined not only by the specific surfaces of the adsorbents but also by their composition and properties. The data obtained by Kryshchenko and Kuznetsov (2003) showed that the clay fractions of the southern chernozem contain four groups of clay minerals: kaolinite, chlorite, mica, and smectite. In the dust fraction of the soils, the content of hydromicas increases by 10–19% compared to the clay fraction, and that of smectites decreases. The content of humus in the dust fraction increases by the same factor. The content of clay minerals in the clay and dust fractions is higher than that in the entire soil. On the other hand, the higher of secondary minerals content in the fraction, lead to the higher its adsorption capacity.

The role of organic matter in the adsorption of HMs by the soils and the particle-size fractions is ambiguous. The soil organic matter has a high exchange capacity. However, in the soils and especially in the fine fractions, it is usually bound to the mineral soil components. Highly condensed humus blocks the medium and fine pores, which significantly reduces the adsorption capacity. Organic molecules are strongly adsorbed at these positions because of their high activity (Kaiser and Guggenberger, 2003). Kurochkina et al. (2002) showed that carboxyl-containing organic molecules are most strongly adsorbed on positively charged surface sites, primarily on the apices and edges of crystals and various surface defects, including medium and fine pore throats.

The analysis of the results (Table 6) showed that the content of exchangeable cations released into solution at the HMs adsorption by the soil decreased in the following series: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{H}^+$. In capacity of the HM cations to displace exchangeable cations from the soil adsorbing complex into the solution, they can be arranged in the following series: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. This series completely corresponded to the adsorption constants of the individual cations from nitrate solutions (Table 2). Thus, the displacement of the exchangeable cations from SAC into solution due to adsorption of HM cations was directly related to the relative affinity of each of them to the soil studied.

When the sorption of HMs increased, the ratio of the sum displaced exchangeable cations to the adsorbed metals ($\Sigma\text{disp. cat.}/C_{\text{ads}}$) decreased (Table 6). During adsorption of copper and lead from nitrate solutions, these ratios were higher than 1 in the entire concentration range. During adsorption of zinc, the ratio of the sum displaced exchangeable cations to the adsorbed Zn at the significant adsorption of the HM by the soil became lower than 1.

The over-equivalent displacement of the exchangeable cations at a relatively low content of HMs in the SAC is explained by the presence of an insignificant content of Ca and Mg carbonates, as well as precipitates of the other soluble Ca^{2+} , Mg^{2+} , Na^+ , and K^+ salts, in the dry soil. The decrease in the ratio of the sum displaced cations to the adsorbed HMs at the increase in the portion of the adsorbed HMs can be related to the adsorption of the associated MeL^+ forms of metal (where L is a single-charged ligand) and the precipitation of difficultly soluble HMs hydroxides localized on separate areas of the soil particles surfaces. The adsorption of charged HM complexes increases the content of adsorbed HM cations and, hence, the denominator of the ratio considered. In addition, the formation of HM associates can significantly affect the mechanisms of the metal adsorption. In particular, acetates can form polymeric complexes such as $\text{Me}^{2+} - \text{CH}_3\text{COO}^- \dots - \text{OH}^- - \text{TM}^{2+} - \text{OH}^-$ on the solid phase surface (Putilina et al., 2009). In fact, this is a new phase, whose effect on the adsorption of HMs is difficult to control by conventional methods. However, these results in an increase in the content of adsorbed HMs even in the absence of other effects.

The probability of such processes was experimentally proved using the analysis of extended X-ray absorption fine structure spectra (EXAFS spectroscopy) (Manceau et al., 1996, 2002; Morin et al., 1999; Pierzynski, 2008). In particular, Pb-organic complexes, plumbojarosite, and lead phosphates were identified in soils, and the possibility of their formation during the fractional analysis of HMs was shown. It was also noted that bidentate complexes with functional groups of aromatic rings are very stable.

Especially low values of the $\Sigma\text{displ.cat.}/C_{\text{ads}}$ (ratio <1) were typical for zinc adsorption. In this case, the mechanism of the zinc interaction with the exchangeable cations differed from those for copper and lead. Zinc was the least associated in the solutions in the specified pH range and occurred almost completely as free cations. The Zn^{2+} cations had a lower relative affinity for the chernozem compared to the Cu^{2+} and Pb^{2+} cations; therefore, they displaced smaller amounts of exchangeable cations and especially Ca^{2+} and Mg^{2+} into the solution. The presence of specific adsorption positions with relatively high affinities for zinc in the SAC favored the adsorption of extra amounts of this element and the acidification of the solution. However, the precipitation of difficultly soluble zinc compounds on the surface was also of importance (Minkina et al., 2008).

Roberts et al. (2003) showed that the surface precipitation of zinc occurs at its concentrations lower than the corresponding solubility products. This can be related to the local pH microheterogeneity due to the cluster matrix structure of the soil particles' surface (Pinskii and Kurochkina, 2006, 2012). It results from the partial protonation of the surface of the soil's clay minerals, which leads in the formation of positively charged cluster matrix structures. In the close vicinity of this surface, an excess of OH^- ions is formed in the solution volume, which results in high local pH values and radically changes the character of the physicochemical processes between the soil surface and the contacting solution.

The formation of willemite (Zn_2SiO_4), kerolite ($\text{Si}_4(\text{Mg}_{2.25}\text{Zn}_{0.75})\text{O}_{10}$), hemimorphite ($\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2$), and zinc sulfide on the surface of the soil particles under waterlogging conditions was proved by EXAFS spectroscopy (Martinez et al., 2006). The localization of these minerals was possible near the surface areas with high pH values. Borda and Sparks (2007) referred to such behavior of HMs as clustering. It accompanies the sorption–desorption of HMs by soils.

An important role in the formation of localized insoluble surface compounds is played by the kinetics of the processes. The adsorption is a relatively rapid process, and the formation of new surface phases is a significantly slower process. It involves not only the adsorption of HMs on the corresponding surface areas but also the transformation of the adsorbed ions, which is slowed down by the interaction with the surface and requires additional energy consumption. Thus, there are many possibilities for the seeming nonequivalence of the HM exchange with exchangeable cations from the SAC, including the precipitation of insoluble compounds localized on the surface of the soil particles. However, these processes should be behind the adsorption processes. In this case, they can be identified from the thorough study of the process's kinetics.

The result obtained is of methodological importance. It indicates the presence of areas with high specific adsorbing capacities for a specific HM (in accordance with its properties) on the surface of the soil particles, which agrees with the earlier concepts of the role of cluster matrix structures in exchange and adsorption processes on the surface of soil particles (Pinskii and Kurochkina, 2006, 2011). The content of exchangeable cations displaced into the solution depends in this case on the adsorbing ion, its relative content in the exchangeable phase, and the presence of surface areas specific to some HM cations.

Conclusion

The isotherms of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption were described by the Langmuir equation in all the cases. The dispersion increase particle-size fractions in similar soils resulted not only in an increase adsorption of HMs, but also to enhancement of their fixation on the surface of the fine particles. Therefore, the adsorption capacity of the studied soils for Cu^{2+} , Pb^{2+} , and Zn^{2+} decreased in the following sequence: clay loamy ordinary chernozem \approx clay loamy southern chernozem > loamy southern chernozem > loamy sandy southern chernozem.

According to the values of the adsorption parameters (C_{max} and k) for the different particle-size fractions, the HM cations formed a sequence analogous to that obtained for the entire soils: $\text{Cu}^{2+} \geq \text{Pb}^{2+} > \text{Zn}^{2+}$. The parameters of the HM adsorption by the same particle-size fractions isolated from the different soils decreased in the following sequence: clay loamy chernozem > loamy chernozem > loamy sandy chernozem. This was related to the qualitative differences in the mineralogy and chemistry of the separated fractions

and the significant effect of their composition and properties on the parameters of the HM adsorption. The analysis of the changes in the parameters of the Cu^{2+} , Pb^{2+} , and Zn^{2+} adsorption by the studied soils and their particle-size fractions showed that the extensive adsorption characteristic – the maximum adsorption (C_{max}) – is a less sensitive parameter characterizing the adsorption capacity of the soils than the intensive characteristic of the process – the adsorption equilibrium constant (k).

The comparative assessment of the adsorbed HMs (C_{ads}) and exchangeable cations displaced into the solution indicated the absence of balance between these values. At low contents of HMs in the SAC, the transition of the over-equivalent amounts of exchangeable cations into the solution took place due to the dissolution of soluble Ca^{2+} , Mg^{2+} , Na^+ , and K^+ salts and the Ca^{2+} and Mg^{2+} carbonates present. At high contents of the adsorbed HMs, the sum of the exchangeable cations displaced into the solution became smaller than the adsorption of HMs, and the $\Sigma_{\text{displ. cat.}}/C_{\text{ads}}$ ratio became lower than 1. This was due to the effect of different factors: the association of HMs with the solution components; the presence of sites specific for HM cations, the sorption on which was not typical for exchangeable cations; and the formation of different new phases localized on the surface of the soil particles.

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References

- Borda, M.J., Sparks, D.L., 2007. Kinetics and mechanisms of sorption - desorption in soils: A Multiscale Assessment. In: A. Violante, P.M. Huang, G.M. Gadd (eds.), *Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soils Environments*. Wiley & Sons. pp. 97–124.
- Kaiser, K., Guggenberger, G., 2003. Mineral surface and soil organic matter. *European Journal of Soil Science* 54, 219–236.
- Karpukhin, A.I., Sychev, V.G., 2005. Complex compounds of soil organic substances and metal ions. VNIIA, Moscow. 186 p. (in Russian).
- Kryshchenko, V.S., Golozubov, O.M., Kolesov, V.V., Rybyanets, T.V., 2008. Data bases on the composition and properties of soils. RSEI, Rostov-on-Don. 145 p. (in Russian).
- Kryshchenko, V.S., Kuznetsov, R.V., 2003. Clay Minerals in Soils of the Lower Don and Northern Caucasus. *Izvestia Vuzov. Severo-Kavkazskii Region. Estestvennie Nauki* 3, 86–92.
- Kurochkina, G.N., Pinskiy, D.L., 2012. Development of a Mineralogical Matrix at the Adsorption of Polyelectrolytes on Soil Minerals and Soils. *Eurasian Soil Science* 45 (11), 1057–1067.
- Kurochkina, G.N. Pinskiy, D.L., 2002. Mechanism of Adsorption of High Molecular Surfactants on Synthetic Analogues of Soil Aluminosilicates. *Eurasian Soil Science* 35 (10), 1046–1057.
- Manceau, A., Boisset, M.C., Sarret, G., Hazemann, R.L., Mench, M., Cambier, P. Prost, R., 1996. Direct Determination of Lead Speciation in Contaminated Soils by EXAFS Spectroscopy. *Environmental Science Technology* 30, 1540–1552.
- Manceau, A., Marcus, M.A., Tamura, N., 2002. Quantitative Speciation of Heavy Metals in Soils and Sediments by Synchrotron X-Ray Technique. In: *Application of Synchrotron Radiation in Low Temperature Geochemistry and Environmental Science. Reviews in Mineralogy and Geochemistry* 49, 341–428.
- Martinez, C.E. Bazilevskaya, K.A. Lanzirotti, A., 2006. Zinc Coordination to Multiple Ligand Atoms in Organic-Rich Surface Soils. *Environmental Science Technology* 40, 5688–5695.
- McBride, M.B., 1989. Reactions Controlling Heavy Metals Solubility in Soils. *Advances Soil Sciences* 10, 2–47.
- Minkina, T.M., Pinskiy, D.L., Samokhin, A.P., Kryshchenko, V.S., Gaponova, Yu.I., Mikailsoy, F., 2009. Effect of Attendant Anions on the Adsorption of Zinc, Copper, and Lead by Chernozem. *Eurasian Soil Science* 42 (5), 516–522.
- Minkina, T.M., Motusova, G.V., Mandzhieva, S.S., Nazarenko, O.G., 2012. Ecological resistance of the soil-plant system to contamination by heavy metals. *Journal of Geochemical Exploration* 123, 33–40
- Minkina, T.M., Motuzova, G.V., Nazarenko, O.G., 2006. Interaction of Heavy Metals with the Organic Matter of an Ordinary Chernozem. *Eurasian Soil Science* 39 (7), 720–726.
- Minkina, T.M., Motuzova, G.V., Nazarenko, O.G., Kryshchenko, V.S., Mandzhieva, S.S., 2008. Forms of Heavy Metal Compounds in Soils of the Steppe Zone. *Eurasian Soil Science* 41 (7), 708–716.
- Morin, G., Ostergren, J.D., Juillot, F. Ildefonse, P., Calas, G., Brown, G.E., 1999. XAPS Determination of the Chemical Form of Lead in Smelter-Contaminated Soils and Mine Tailings: Importance of Adsorption Process. *American Mineralogist* 84, 420–434.
- Perelomov, L.V., Pinskiy, D.L., 2003. Mn, Pb, and Zn Compounds in Gray Forest Soils of the Central Russian Upland. *Eurasian Soil Science* 36 (6), 610–618.

- Pierzynski, G.M., Baker, L.R., Hettiarachchi, G., Scheckel K.G., 2008. The use of soil amendments for the remediation of heavy-metal contaminated sites. In: *Proceedings of the 14th International Conference on Heavy Metals in the Environment*. Z.S. Chen, D.Y. Lee, and T.S. Lin (eds.), November 16-23, 2008. National Taiwan University, Taipei, Taiwan. pp. 1-3.
- Pinskii, D., 2011. Clusters in Soils. In: Jan Glinsky, Jozef Horabik, Jerzy Lipiec (eds.), *Encyclopedia of Agrophysics*. Springer-Verlag, Heidelberg. pp. 135-138.
- Pinskii, D.L., Minkina, T.M., Gaponova, Yu.I., 2010. Comparative analysis of mono- and polyelement adsorption of copper, lead, and zinc by an ordinary chernozem from nitrate and acetate solutions. *Eurasian Soil Science* 43 (7), 748-756.
- Pinskii, D.L., Kurochkina, G.N., 2006. Evolution of Concepts of the Physicochemical Sorption Capacity of Soils. In: *Soil Processes and the Spatial-Temporal Organization of Soils*. Nauka, Moscow. 295-311 (in Russian).
- Plyaskina, O.V. Ladonin, D.V., 2005. Heavy Metal Compounds in Particle-Size Fractions of Some Soil Types. *Vestnik Moskovskogo Universiteta. Seria 17: Pochvovedeniue* 4, 36-43.
- Putilina, V.S., Galitskaya, I.V., Yuganova, T.I., 2009. Adsorption of heavy metals by soils and Rocks. Characteristics of sorbents and conditions, parameters, and mechanisms of adsorption. *Analytic Review*. GPNTB SO RAN, Novosibirsk. 155 p (in Russian).
- Roberts, D. Scheinost, A. Sparks, D., 2003. Zinc Speciation in Contaminated Soils Combining Direct and Indirect Characterization Methods. In: H.M. Selim, and W.L. Kingery (eds.) *Geochemical and Hydrological Reactivity of Heavy Metals in Soils*. CRC Press, Boca Raton, FL. 376 p.
- Scheinost, A.C. Kretzchmar, R.S., Pfister, S., 2002. Combining Selective Sequential Extractions, X-Ray Adsorption Spectroscopy, and Principal Component Analysis for Quantitative Zinc Speciation in Soil. *Environmental Science Technology* 36, 5021-5028.
- Shaimukhametov, M.Sh., 1993. On the method of determination of adsorbed Ca and Mg in chernozemic soils. *Pochvovedenie* 12, 105-111.
- Sokolov, A.V. (ed.), 1975. *Agrochemical Methods of Soil Studies*. Five edition. Akad. Nauk USSR, Moscow. 656 p (in Russian).
- Titova, N.A., Travnikova, L.S., Kakhnovich, Z.N. Sorokin, S.E., Schulz, E., Korschens, M., 1996. Heavy metal content in various particle-Size and Density Fractions of Soils. *Eurasian Soil Science* 29(7), 820-830.
- Vadyunina, A.F., Korchagina, Z.A., 1986. *Methods for Studying Soil Physical Properties*. Third edition. Agropromizdat, Moscow. 416 p (in Russian).
- Wong, J.W.C., Li, K.L., Zhou, L.X., Selvam, A., 2007. The Sorption of Cd and Zn by Different Soils in the Presence of Dissolved Organic Matter from Sludge. *Geoderma*. 137. 310-317.
- Zyrin, N.G., Chebotareva, N.A., 1989. To the question of forms of copper, zinc, and lead in soils and their availability for plants. In: A.I. Karpukhin (ed.). *The contents and forms of microelement compounds in soils*. Mosk. Univ., Moscow. 350-386 (in Russian).